

Particles and Radicals in Amorphous Silicon Deposition

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ABSTRACT

Silicon-based particles, which form in silane discharges used for chemical vapor deposition (CVD) of hydrogenated amorphous silicon (a-Si:H) photovoltaics, are measured with light scattering. We show that pressure, RF voltage, temperature, and disilane produced in the discharge have a major influence on particle growth and density, but a comparatively minor influence on film growth rate. Si_xH_n radicals, the primary cause of a-Si:H film growth, are being measured by threshold ionization mass spectroscopy under hot wire CVD conditions. The fluxes of silicon and hydrogen to the substrate, and their implications to hot wire CVD of a-Si:H and $\mu\text{c-Si}$, will be presented.

1. Introduction

Silicon and hydrogen-based particles form in silane-containing discharges, and they can influence both the discharge and a-Si:H-based, photovoltaic (PV) properties. They form as negative ions, which are trapped in the discharge, and grow from reactions with silicon-containing radicals. As particles are dragged by gas flow to the edges of the plasma, many small particles (mostly containing $<10^4$ Si atoms) are neutralized and escape into the growing device layers. However, many accumulate at the downstream plasma edge until they grow to micrometer sizes and escape in bursts toward pumps. The latter do not incorporate into films, but they influence the discharge impedance and power loading. We have measured the behavior of both types of particles, but here only present data related to the smaller particles that incorporate into films.

Neutral radicals produce most deposition of a-Si:H films in discharge CVD, and all of the deposition in hot wire CVD. The material properties are sensitive to the radical mixture; for instance micro-crystalline versus amorphous films result from changes in the H/SiH_n ratio. To improve understanding of how radical fluxes depend on deposition conditions, we are measuring radical fluxes to the substrate in a hot wire CVD chamber. We utilize threshold ionization mass spectroscopy (TIMS), which is capable of detecting H and all Si_xH_n radicals in small concentrations. However, the data must be coupled with detailed analysis to establish the reactions on the hot wire, in the gas, and on the chamber services. Data and ongoing analysis will be presented.

2. Particle Results

Our particle-scattering measurements yield average particle diameter (d_p) above the substrate from

afterglow diffusion and effective particle density (n_p) from scattering intensity. Since particles grow above the substrate for different times in different PV production reactors, we measure d_p and n_p versus discharge operating time. We find that, after a brief induction period, d_p grows linearly with time at a rate G_p . Although only $d_p > 6$ nm particles are observable by scattering, and many more smaller particles incorporate into films, we can infer the density of the smaller, precursor particles from the density of their later, larger form. G_p and n_p , hence particle incorporation into films, are very sensitive to discharge temperature (T), silane density (n_1), RF voltage (V_{RF}) and disilane (density n_2) produced by the discharge chemistry. In essence, without H_2 dilution or temperature gradients, particle growth rates typically vary as $T^{-20} n_1^7 n_2^{35} V_{\text{RF}}^8$. An example of the observed T and n_1 dependence of G_p is shown in Fig. 1.

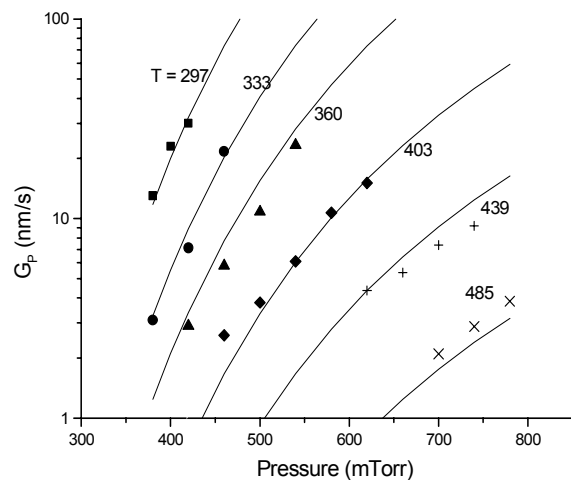


Figure 1. Temperature and silane pressure dependence of particle growth rate, at fixed RF voltage and film deposition rate (~ 0.3 nm/s).

Within the measured range of particle diameters (6-50 nm), density decreases with increasing d_p , indicating major particle loss into films. This typically varies as d_p^{-m} with $m=2-4$, with $n_p(d_p = 16 \text{ nm}) \cong 10^7 \text{ cm}^{-3}$ in pure silane.

A second, unexpected discovery is that as disilane builds up in the vapor, due to the $\text{SiH}_2 + \text{SiH}_4$ reaction, this greatly increases G_p and n_p . This disilane buildup occurs in all silane discharges, typically reaching a steady state disilane density that is $\sim 5\%$ of the silane density. This relatively small amount of disilane has a profound

influence, as shown in Figs. 2 and 3, where G_p and n_p are plotted versus the two densities (in pressure units).

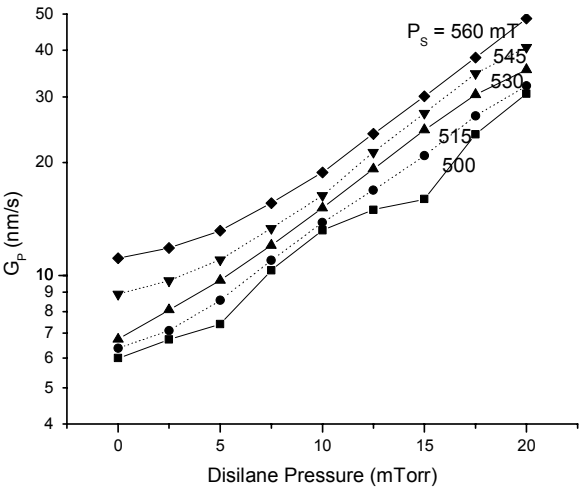


Figure 2. Particle radius growth rate, versus disilane and silane pressures, for a 130°C, RF discharge in 130 mTorr of H₂ plus the indicated pressures silane and disilane. The RF voltage is constant, as is the film growth rate of ~ 0.3 nm/s.

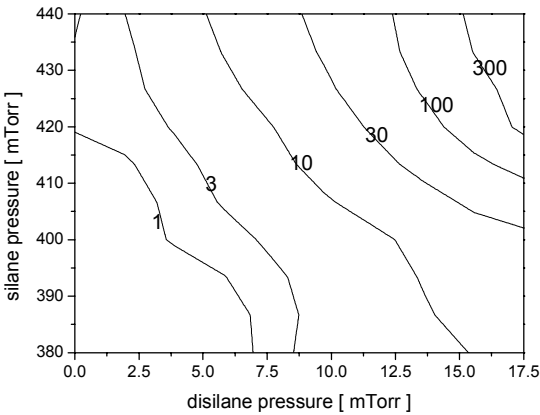


Figure 3. Density of 16 nm diameter particles, in 10⁷/cm³ units, versus silane and disilane pressure, for the discharge conditions of Fig. 1.

When T gradients occur in a discharge, strong thermophoresis forces push particles toward colder surfaces. For typical reactor conditions ($T_{\text{substrate}} - T_{\text{RF electrode}} > 50^\circ\text{C}$) this can prevent almost all $d_p > 4$ nm particles from reaching the substrate. Nonetheless, there is almost no way to prevent $d_p < 2$ nm particles from incorporating into films.

With H₂ dilution and typical a-Si:H deposition conditions, G_p and n_p are larger than for a pure-silane inlet flow, and incorporation of $d_p > 2$ nm particles is correspondingly increased. H atom density is higher in the discharge center where particles reside, compared to at the

substrate, so for “near-the-edge” dilution conditions these particles are expected to be crystalline. This can be advantageous, as in seeding micro-crystalline layers, but it should be realized and the importance of T gradients in controlling this micro-crystal shower should be appreciated.

3. Radicals in Hot-Wire CVD

From the work of Molenbroek et al. [1], it is known that obtaining high film quality by hot wire CVD requires sufficient n_i to prevent most Si atoms from reaching the substrate, but not so much n_i that many heavy radicals (Si_xH_n with $x > 1$) form and produce film. However, these radical behaviors are only indirectly inferred, and the actual species and the dependence on hot-wire temperature (T_F) and silane exposure, surface temperatures and H₂ dilution is not known, nor are the actual higher silane species and their dependence on conditions known. Thus, we are measuring these radicals now by TIMS. This is done with a specially designed, radical-ionization electron beam and ion collection optics, to yield strong discrimination against the SiH_n^+ ions resulting from dissociative ionization of silane.

Our present measurements concentrate on the Si flux to the substrate, versus conditions such as silane, hydrogen and argon pressure and T_F . We observe that in pure silane at typical operating conditions (pressure ~ 10 mTorr, gap ~ 4 cm) almost all Si indeed reacts before reaching the substrate. In contrast, adding an inert gas, which cools many Si atoms before they collide with silane, allows a significant Si fraction to reach the substrate, indicating a reaction barrier. These and other influences on Si flux to the substrate will be presented.

REFERENCES

[1] E. Molenbroek, A. Mahan, and A. Gallagher. “Mechanisms influencing ‘hot-wire’ deposition of hydrogenated amorphous silicon,” *J. Appl. Phys.* **82** (1997) pp. 1909-1917.